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(54) Title: PROCESS OF MAKING CELLULOSIC FIBERS INCLUDING PTFE

(57) Abstract: The present invention is directed to a method for making solution spun fibers having decreased coefficient of friction and other improved properties such as wear resistance and the like, when compared to conventional solution spun fibers. In the method of the present invention, polytetrafluoroethylene (PTFE) is incorporated into the fiber-forming substance during the solution spinning process before passing through the spinneret. PTFE that is useful in the present invention includes PTFE powder that is dispersible to low micron or submicron particle size and aqueous or organic dispersions of such highly dispersible PTFE powder. The present invention is also directed to fabrics, textiles, and other articles of manufacture formed from the PTFE-enhanced solution spun fibers of the present invention.

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## PROCESS OF MAKING CELLULOSIC FIBERS INCLUDING PTFE

### SPECIFICATION

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#### CROSS REFERENCE TO RELATED APPLICATION

The present application claims priority from U.S. Provisional Patent Application No. 60/415,005 filed October 1, 2002, the disclosure of which is incorporated herein by reference in its entirety.

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#### FIELD OF THE INVENTION

The present invention generally relates to a method for incorporating highly dispersible polytetrafluoroethylene (PTFE) powder into solution spun synthetic fibers so that the resulting fibers have improved properties generally associated with PTFE, including, for example, low coefficient of friction, improved wear resistance, hydrophobicity, improved stain resistance and improved light stability and UV-light resistance, when compared to conventional solution spun synthetic fibers. The present invention further relates to solution spun fibers with incorporated PTFE made by the method described herein, and to textiles, fabrics, and other articles of manufacture that are made from these solution spun synthetic fibers.

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#### BACKGROUND OF THE INVENTION

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In the textile industry, apparel manufacturers and fiber producers are constantly attempting to modify or enhance the basic composition of each generic type of synthetic fiber, both chemically and physically, in order to produce desirable fiber variations. Fiber variations are sought so that the improved fibers provide softer feel, greater comfort, brighter and longer lasting colors, better warmth or cooling, better moisture transport or wicking, and better blending properties when blending with other fibers. See e.g., "FabricLink, Fabric University – Fabric Producers and Trademarks," <<http://www.fabriclink.com/Producers.html>>. Thus, a constant need

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exists in the art of fiber production for new and innovative ways to improve the properties of synthetic fibers.

Various manufacturing processes are known in the art for making synthetic fibers. Many synthetic fibers are produced by extrusion processes, in which  
5 a thick viscous liquid polymer precursor or composition is forced through tiny holes of a spinneret to form continuous filaments of semi-solid polymer. As the filaments emerge from the holes of a spinneret, the liquid polymer converts first to a rubbery state which then is solidified. The process of extruding and solidifying filaments is generally known as spinning. One common method of spinning filaments of  
10 manufactured or synthetic fibers is generally known as "solution spinning" or "wet spinning."

Typically, solution spinning or wet spinning processes are employed with fiber-forming substances that have been dissolved in a solvent. The spinnerets forming the filaments are submerged in a wet chemical bath, and as the filaments of  
15 the fiber-forming substances emerge from the spinnerets, they are induced to precipitate out of the solution and solidify. Synthetic fibers that are commonly produced by solution spinning processes include rayon fibers, acrylic fibers, aramid fibers, such as Kevlar® para-aramid fibers, modacrylic fibers, and spandex fibers, among others. These synthetic fibers are made from fiber-forming substances, which  
20 primarily are soluble cellulose or soluble compounds of cellulose.

Rayon, which is one of the most common synthetic fibers produced by solution spinning, is defined as a manufactured fiber composed of what is known as "regenerated" cellulose in which substituents have replaced not more than 15% of the hydrogens of the hydroxyl groups. See e.g., Rules And Regulations Under  
25 The Textile Fiber Products Identification Act, 16 CFR Part 303. In most rayon production processes, purified cellulose is chemically converted into a soluble compound, and a solution of this compound is passed through the spinneret to form soft filaments that are then converted or "regenerated" into almost pure cellulose. Because of this reversion of the soluble compound into cellulose, rayon  
30 is commonly referred to as a regenerated cellulose fiber.

Additives (e.g., dyes or surfactants) may be added to the fiber-forming substance (such as cellulose) prior to extrusion in order to improve the quality of the resulting solution spun fibers. Until the present invention, however, it was not contemplated that the addition of polytetrafluoroethylene (PTFE) powder may be feasible or of benefit in making solution spun fibers. In particular, it was not shown that addition of PTFE powder that is dispersible to low micron or submicron particle size or where the PTFE powder particles have a primary particle size that is low micron or submicron, to the fiber-forming substance for a solution spun fiber was feasible.

It is generally known that PTFE provides characteristics such as improved slipperiness and non-wettability to other materials into which it is incorporated. PTFE is useful when in a powder form or a dispersion form for this purpose. Dry PTFE powder products are known in the art and are generally available in the industry. Several manufacturers in the fluoropolymer industry produce PTFE powders, and some of these manufacturers describe the PTFE particle size in their powders as being "submicron" or capable of being dispersed to submicron size.

A wide array of end uses exists for small particle size or submicron PTFE. For example, small amounts (e.g., about 0.1 to 2% by weight) of powdered PTFE may be incorporated into a variety of product compositions to provide favorable and beneficial characteristics. In inks, incorporated PTFE provides excellent mar and rub resistance characteristics. In cosmetics, incorporated PTFE provides a silky feel. In sunscreens, incorporated PTFE provides increased shielding from UV rays or increased SPF (sun protection factor). In greases and oils, incorporated PTFE provides superior lubrication. In coatings and thermoplastics, incorporated PTFE provides improved abrasion resistance, chemical resistance, weather resistance, water resistance, and film hardness.

Other, more specific end uses for submicron PTFE powders and dispersions include, for example, incorporation of a uniform dispersion of submicron PTFE particles into electroless nickel coatings to improve the friction and wear characteristics of such coatings (see e.g. Hadley et al., *Metal Finishing*, 85:51-53 (December 1987)); incorporation of submicron PTFE particles into a surface finish

layer for an electrical connector contact, wherein the PTFE particles provide wear resistance to the surface finish layer (U.S. Patent No. 6,274,254 to Abys et al.); incorporation of submicron PTFE particles in a film-forming binder as a solid lubricant in an interfacial layer, wherein the interfacial layer is part of an optical waveguide fiber (U.S. Patent No. 5,181,268 to Chien); incorporation of a submicron PTFE powder (along with a granulated PTFE powder and  $\text{TiO}_2$ ) in a dry engine oil additive, wherein the incorporated PTFE increases the slip characteristics of the load bearing surfaces lubricated by the additive (U.S. Patent No. 4,888,122 to McCready); and, combination of submicron PTFE particles with autocatalytically-applied nickel/phosphorus for use in a surface treatment system for metals and metal alloys, wherein the PTFE imparts lubrication, low friction, and wear resistance to the resulting surface ("Niflor Engineered Composite Coatings," Hay N., International, Ltd. (1989)). Additional specific examples of end uses for PTFE involve incorporation of PTFE into engine oils, uses of PTFE as a thickener in greases, and use of PTFE as an industrial lubricant additive. Willson, *Industrial Lubrication and Tribology*, 44:3-5 (March/April 1992).

The beneficial effects imparted to the application or end use system by the addition or incorporation of PTFE particles derive from the advantageous chemical and physical properties of PTFE. Notably, PTFE is chemically inert, physically smooth (i.e. has a low coefficient of friction) and hydrophobic. In the many applications or end uses incorporating submicron PTFE powders and submicron PTFE dispersions (such as the end uses described above), the beneficial properties of PTFE are propagated through out the application or end use product composition. In addition, because submicron PTFE particles have a low particle size, they possess a significantly higher ratio of surface area to weight when compared to larger PTFE particles. Thus, submicron PTFE particles are better able to supply their useful effects to a desired application system than the same weight of larger PTFE particles.

In view of the foregoing of discussion on the constant urge in the fiber industry for making better synthetic fibers having improved properties and the usefulness of incorporating PTFE in various applications, it is evident that a general need exists in the fiber making art for incorporating PTFE in to synthetic fibers. It

particular, it may be commercially desirable, for example, to have fibers that are spun by a solution spinning process possess the improved properties associated with PTFE. Thus, a specific need exists for a convenient and inexpensive PTFE powder that is dispersible to low micron or submicron particle size that can be incorporated into  
5 fiber-forming substances that are used in making solution spun fibers. Furthermore, a need exists for a method of incorporating such low micron or submicron PTFE particles uniformly and permanently throughout a solution-spun fiber as opposed to mere surface treatments or coatings. The uniformity and permanence of the PTFE distribution through the body of a fiber may ensure that textiles, fabrics and clothing  
10 made from the solution spun fibers will not lose, over time, the enhanced properties associated with PTFE because of surface wear and tear. The present invention addresses these and other needs.

### SUMMARY OF THE INVENTION

15 The present invention relates to a novel method by which polytetrafluoroethylene (PTFE) is incorporated into a synthetic solution spun fiber so that the resulting fiber has many improved characteristics and properties when compared to conventional solution spun fibers.

20 In the present method, PTFE powder that is dispersible to low micron or submicron particle size first is added into a fiber-forming substance (such as cellulose) feed, which is suitable for solution spinning of fibers. Subsequently, the PTFE-containing fiber-forming substance or feed is solution spun into filaments or fibers. The resulting filaments or fibers contain PTFE particles dispersed therein.  
25 The PTFE particles may be uniformly or homogeneously dispersed in the bodies of the resulting filaments or fibers. The resulting filaments or fibers have the improved properties associated with PTFE. For example, the solution spun fibers resulting from the method of the present invention exhibit a significant decrease in the coefficient of friction when compared to conventional solution spun fibers.

30 The use of low micron or submicron particle size PTFE powder as an additive to the fiber-forming substances used to make certain synthetic fibers is also important in that the added PTFE improves the non-wetting properties of the fibers

and textiles made from such fibers. Thus, fibers with incorporated PTFE ("PTFE-enhanced fibers") may be useful in industrial textiles that are used in articles or products that are used for filtration and dewatering processes. Such PTFE-enhanced fibers also may be advantageously used in producing carpets, fabrics for sportswear and outerwear, hot-air balloons, car and plane seats, umbrellas, and the like. Furthermore, the fibers of the present invention may be advantageously used to make tightly woven fabrics for use in parachutes, boat sails, and similar applications. A combination of a tight weave and the hydrophobic properties of the PTFE-enhanced fiber may provide a textile or fabric for clothing that is both water-repellent and breathable. The inclusion of PTFE-enhanced fibers into such textiles also may beneficially result in other advantages, such as the textile articles being easier to clean.

The method of the present invention is useful in that the resulting PTFE-enhanced solution spun fibers have many improved properties when compared to conventional synthetic solution spun fibers. Some of these improved properties include but are not limited to the following: lower coefficient of friction; reduced wettability; improved stain resistance; improved washability; improved opacity; enhanced protection from ultraviolet radiation (UV), which increases the light-fastness and the lifetime of the fiber or fabric; increased color fastness; reduced gas permeability; better abrasion resistance; tighter weave; improved wear index; increased flexibility of the fiber; decreased scroop (where scroop generally refers to sounds of rubbing made by certain fabrics); and lowered amounts of wrinkling when the PTFE-enhanced fibers are incorporated into a fabric or clothing article.

Additionally, not only does the method of the present invention result in improved solution spun fibers, but also the method serves to significantly improve the overall processes by which synthetic fibers are typically made. For example, the increased lubricity or slipperiness of the fiber-forming substance due to the addition of PTFE in it may result in lower production times for fiber production, significantly increased processing speeds, increased throughput rates and overall production rates. The increased lubricity of the fiber-forming materials due to the PTFE addition also

may give a longer lifetime to the fiber-making equipment, and provide overall savings in energy that is expended in running the fiber-making equipment.

### **DETAILED DESCRIPTION OF THE INVENTION**

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The present invention relates to a method for making improved solution spun fibers, wherein the fibers are more wear resistant and have a lower coefficient of friction than conventional solution spun fibers that are known in the art. The inventive method improves the quality of a fiber by introducing PTFE that is dispersible to low micron or submicron particle size into the fiber-forming substance from which the fiber is made by a solution spinning process. The PTFE-enhanced solution spun fibers that are made by the method, exhibit, among other properties, increased wear resistance, stain resistance, water resistance, and a significantly decreased coefficient of friction, when compared to conventional solution spun fibers known in the art.

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An important objective of the present invention is to incorporate PTFE throughout a solution spun fiber so that the fiber contains a uniform distribution PTFE through its material body. Thus all sub regions or sections of the fiber have the enhanced properties afforded to the fiber by PTFE. This is in comparison or contrast to other processes and fibers known in the art in which PTFE is only incorporated in the surface layers of fibers or applied to solution spun fibers (or fabrics made from such fibers) as a surface coating.

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In preferred embodiments of the method of the present invention, the following types of PTFE are useful: PTFE powder that is dispersible to submicron particle size; PTFE powder that is dispersible to low micron particle size; aqueous or organic dispersions of PTFE powder that are dispersible to submicron particle size; and aqueous or organic dispersions of PTFE powder that is dispersible to low micron particle size. One specific type of PTFE that may be used in the method of the present invention is described in co-assigned International Patent Application No. PCT/US03/07978 filed on March 14, 2003, which is hereby incorporated by reference herein in its entirety.

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In the present description, the designation "submicron particle size" indicates that a given quantity of PTFE powder disperses in isopropyl alcohol (IPA) such that more than about 90%, preferably, more than about 95%, and more preferably, more than about 99% of the PTFE particles have a particle size that is less than about 1.00  $\mu\text{m}$ . Furthermore, the designation "low micron particle size" indicates that a given quantity of PTFE powder disperses in isopropyl alcohol (IPA) such that about 95% or more of the PTFE particles have a particle size that is less than about 10.00  $\mu\text{m}$ .

The dispersibility of the PTFE powder down to low micron or submicron-sized particles may be important for unhindered practice of solution spinning processes. These small size PTFE particles may pass through spinneret holes with ease, unlike large sized PTFE particles that can clog spinnerets making fiber formation difficult. It is also envisioned that the method of the present invention allows for PTFE that is dispersible to low micron particle size to be used in higher denier fibers, while PTFE that is dispersible to submicron particle size will be useful for forming both low and high denier fibers. The PTFE particles may be uniformly or homogeneously dispersed through the bodies of the fiber of any denier size.

The dispersibility of the PTFE particles in a powder may be determined by dispersing an amount of the PTFE powder in isopropyl alcohol (IPA). Then by conventional particle size analysis (e.g., light scattering analysis), an indication of the mean particle size and the particle size distribution of the PTFE powder may be obtained. Thus a user can verify or confirm, for example, if a sample of PTFE powder is completely (100%) dispersible to submicron in size or otherwise suitable for use in solution spinning processes.

As mentioned above, aqueous or organic dispersions of PTFE that is dispersible either to submicron particle size or low micron particle size may be used in the solution spinning processes. PTFE dispersions that are most useful in the present method may include from about 5% to about 60% PTFE by weight. A pelletized master batch having an appropriate concentration of PTFE (e.g., 5% to 60%) may optionally be used for this purpose. Alternatively, dry PTFE powder that is dispersible either to submicron or low micron particle size may be dispersed directly

into the fiber-forming substance (such as cellulose). In certain preferred embodiments of the method of the present invention, an aqueous or organic dispersion of PTFE that is dispersible either to submicron particle size or low micron particle size is first provided. The steps of an inventive process for making a PTFE-enhanced solution spun fiber are then employed.

Conventional solution spinning processes for making rayon fibers involve a number of steps in processing or preparing fiber-forming material as feed for solution spinning through spinnerets. These steps as commonly described in the literature as the steps of steeping, pressing, shredding, aging, xanatahation, dissolving, ripening, filtering, and degassing, and wet bath spinning. See e.g.,  
www.fibersource.com/f-tutor/rayon.htm. The processes for making an PTFE-enhanced solution spun fiber advantageously may be based on conventional solution spinning processes, with appropriate or modifications. The steps of exemplary processes for making the PTFE-enhanced solution spun fibers are described below, using for convenience the same terminology that is commonly used to describe the steps of the conventional solution spinning processes for rayon.

The rayon making processes typically utilize cellulose as a raw material. Specifically, purified cellulose is used as the fiber-forming material in the production of rayon. The purified cellulose is prepared from specially processed wood pulp and is sometimes referred to as "dissolving cellulose" or "dissolving pulp" to distinguish it from lower grade pulps that are used for papermaking or other purposes. Dissolving cellulose is characterized as having a high  $\alpha$ -cellulose content, which means that the cellulose consists mainly of long-chain molecules and is relatively free from lignin and hemicelluloses or other short-chain carbohydrates. The purified cellulose is often obtained in the form of cellulose sheets.

In preparing the raw material feed for solution spinning of rayon fibers, the cellulose sheets are first wetted with a wetting agent. This wetting step provides one way of incorporating PTFE according to the present invention. In conventional spinning processes, the wetting agent is usually water. However, in one embodiment of the present invention, the cellulose sheets may be wetted with an aqueous dispersion of PTFE that is dispersible either to submicron particle size or low micron

particle size. The PTFE may be incorporated into the cellulose sheets mechanically, for example, by mixing, stirring or blending. As shown below, in alternative embodiments, the PTFE may be incorporated into the cellulose at any process step or point prior to the spinning of the rayon filaments.

5                   In the next processing step "steeping", the wetted cellulose sheets (that were wetted with an aqueous dispersion of highly dispersible PTFE) are saturated with a solution of caustic soda (or sodium hydroxide). The wetted cellulose sheets are allowed to steep for sufficient time for converting some of the cellulose into "soda cellulose" (or the sodium salt of cellulose). During the next process step called  
10 "pressing," the soda cellulose is squeezed mechanically to remove excess caustic soda solution.

The soda cellulose is then mechanically shredded to small size fragments to increase its active surface area, and thereby to make the soda cellulose more soda cellulose more processible. This shredded cellulose is typically referred to  
15 as "white crumb." At the next step "aging", this white crumb is allowed to stand in contact with the oxygen of the ambient air. The contact with the oxygen partially oxidizes the white crumb (because of the high alkalinity of the white crumb) and degrades the cellulose in the white crumb to lower molecular weights (i.e. shorter chain length molecules). The aging times and degradation conditions are carefully  
20 controlled to produce chain lengths that are short enough to give manageable viscosities in the spinning solution, but still long enough to impart good physical properties to the solution spun fiber product.

After the above-described "aging" process, the white crumb is placed into a churn or some other mixing vessel and is treated with gaseous carbon disulfide  
25 ( $\text{CS}_2$ ) in a "xanthation" step. In certain embodiments of the present invention, the incorporation of the aqueous dispersion of the PTFE may conveniently occur just after the aging process, as the white crumb is placed into the churn and/or being treated with  $\text{CS}_2$  in the churn. The soda cellulose reacts with the  $\text{CS}_2$  to form xanthate ester groups. The  $\text{CS}_2$  also reacts with the alkaline medium to form inorganic impurities,  
30 which give the cellulose mixture a characteristic yellow color. This material that results from the xanthation process is typically referred to as "yellow crumb."

Subsequently, the yellow crumb is dissolved in aqueous caustic solution in a "dissolving" step. In certain embodiments of the present invention, the aqueous dispersion of highly dispersible PTFE may be conveniently added at this stage to the yellow crumb. The yellow crumb is not completely or fully soluble at this stage. Specifically, because the cellulose xanthate solution or suspension has such a high viscosity, it is typically termed the "viscose." The viscose is allowed to stand for a period of time to "ripen." During ripening, two important chemical processes occur: redistribution and loss of xanthate groups.

Next, the viscose is filtered to remove undissolved or undispersed materials that might disrupt the spinning process or cause defects in the rayon filament. In embodiments of the present invention where the highly dispersible PTFE has already been incorporated into the viscose by this stage, this "filtering" step is properly controlled, e.g., by using suitable filter sizes, so that the added PTFE particles are not filtered out of the viscose. Additionally, the viscose may be degassed, i.e. bubbles of air entrapped in the viscose may be removed, prior to extrusion to avoid air-voids or weak spots in the fine rayon filaments.

The aged and degassed viscose can be used as feed to spinnerets for solution spinning fine filaments of PTFE-enhanced rayon. Specifically, the viscose may be forced through a spinneret, which may be a device resembling a shower head with a plurality of small diameter channels or holes. In certain embodiments of the present invention, the aqueous dispersion of highly dispersible PTFE may be conveniently added to the viscose as the viscose is about to enter the spinneret. Each hole of the spinneret generates a fine filament of the viscose. As the viscose exits the spinneret as filaments, it comes in contact with the chemicals in the wet chemical bath. These chemicals may be a solution containing sulfuric acid, sodium sulfate, and usually  $\text{Zn}^{+2}$  ions. Several processes may occur at this point, which cause the cellulose in the filaments to be regenerated and to precipitate from the solution. For example, water diffuses out from the extruded viscose to increase the concentration in the filament beyond the limit of solubility. The xanthate groups in the filaments form complexes with the  $\text{Zn}^{+2}$  ions, which draw the cellulose chains together. The acidic spin bath converts the xanthate functions

into unstable xanthic acid groups, which spontaneously lose CS<sub>2</sub> and regenerate the free hydroxyls of cellulose. The result is the formation of PTFE-enhanced fine filaments of cellulose, or rayon.

After the PTFE-enhanced rayon filaments are formed, the filaments  
5 may be stretched while the internal cellulose molecular chains remain relatively immobile. This may cause causes the molecular chains to stretch out and to orient along the axis of the filaments giving them attributes necessary for use as textile fibers. The PTFE-enhanced rayon fibers are then washed to remove salts and other water-soluble impurities that are present in freshly regenerated rayon. The PTFE-  
10 enhanced rayon filaments then may be cut to suitable lengths as necessary for intended use. For example, if the PTFE-enhanced rayon is to be used as staple (*i.e.*, discrete lengths of fiber), the group of filaments, often termed "tow," may be passed through a rotary cutter to provide a fiber, which can be processed in much the same way as a cotton fiber.

15 The PTFE-enhanced solution-spun fibers produced by such a method may then be manufactured into a fabric or a textile. Such fabric or textile may have the enhanced properties typically associated with the addition of PTFE to articles. For example, the fabric or textile may exhibit a significantly decreased coefficient of friction, which can be an advantageous property of fabrics or textiles that are intended  
20 for apparel used in sports or recreational activities. Other advantageous properties of the solution-spun fibers of the present invention include the exceptional wear resistance exhibited by the PTFE-enhanced fibers.

Specifically, the solution-spun fibers and/or the fabrics made from the fibers of the present invention may be wear tested to determine the wear resistance of  
25 the fibers. The wear testing may include Taber testing, Mace testing, and Pilling tests. Similarly, tests may be performed to determine the tenacity of the fabric, the elongation of the fabric, and the draw. Generally, the same full range of tests that are commonly used to analyze the properties of solution -spun fibers in the industry may be employed to test the fibers of the present invention. Tests used in other industries  
30 and other scientific test methods can also be used to characterize the fibers and fabrics of the present invention.

The method and compositions of the present invention may be better understood through the working Examples detailed below. These Examples are intended to illustrate the invention and should not be construed as limiting the invention in any way.

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### EXAMPLES

#### Example 1: Production of PTFE-Enhanced Rayon Fiber:

10 In the present Example, PTFE-enhanced rayon fibers were made according to the method of the present invention for comparison with conventional rayon fibers. Specifically in this Example, three types of cellulose were tested initially to determine their suitability for making rayon: cosmetic cotton balls that are available in drug stores, and two types of wood cellulose products. Samples of all  
15 three cellulose types were steeped. After both of the wood cellulose pulp samples were steeped, they gave out undesirable brown-colored matter probably because of the presence of lignin, hemicelluloses and other short-chain carbohydrates. Conversely, the initial testing of the cosmetic cotton balls resulted in a clean, orange-colored cellulose xanthate solution having the requisite high viscosity. According to  
20 these test results, only the cosmetic cotton ball raw material was selected for use in further experiments.

In a further experiment, cosmetic cotton ball cellulose material was mechanically shredded to increase its surface area and to thereby make its cellulose easier to process. Then, the cellulose was steeped. Specifically, 1 gram of shredded  
25 cellulose ("Sample 1") was wet with 5 mL of water in a beaker. Next, 50 ml of a 15% sodium hydroxide solution was added to the beaker under continuous stirring to form soda cellulose. The mixture was allowed to stand or steep for about one hour. Visual observations of this mixture revealed that the steeped mixture had the appearance of "white crumb" in a transparent liquid.

30 Another 1 gram of the shredded cellulose ("Sample 2") was wet with 5 ml of an aqueous dispersion of submicron PTFE in a beaker. The specific the PTFE used in this Example was a PTFE product that is commercially available from assignee Shamrock Technologies, Inc. under the trade name "NanoFLON W50C." In

further processing similar to the case of Sample 1 above, 50 mL of a 15% sodium hydroxide solution was then added to Sample 2 under continuous stirring. The Sample 2 mixture was also allowed to steep for one hour. Visual observations of the Sample 2 mixture revealed that the steeped mixture had the appearance of "white crumb" in cloudy liquid, which is consistent with the formation of a soda cellulose/PTFE mixture.

Next, the soda cellulose of Sample 1 and the soda cellulose/PTFE of Sample 2 were each placed on separate mesh filters and squeezed mechanically to remove any excess caustic soda solution and form "white crumb". For Sample 1, the removed solution was slightly yellow and cloudy, whereas for Sample 2, the removed soda solution appeared more like a PTFE suspension.

Then, 25 mL of CS<sub>2</sub> was added to each "white crumb" mixture in beaker under continuous stirring in a "xanthation" step. Both Samples 1 and 2 were stirred for 3 hours. After 3 hours, the white crumb of Sample 1 had changed in color to orange-yellow and had a highly swollen appearance in a transparent medium. The white crumb of Sample 2 had changed in color to whitish-yellow and was not transparent. Next, excess of liquid was carefully removed from each of the samples, leaving behind what is typically termed as the "yellow crumb" for each of the two samples.

The Sample 1 and Sample 2 yellow crumbs were each dissolved in 15 ml of a 15% NaOH solution gradually under stirring. After dissolution, Sample 1 resulted in a bright orange viscose solution. In contrast, Sample 2 resulted in a faint orange solution. The two viscoses produced from Samples 1 and 2 were allowed to stand for one hour to "ripen," and loose bubbles (that may have been introduced into each viscose by stirring) were removed by degassing.

The Sample 1 and 2 viscoses were then subject to a laboratory simulation of solution spinning. Specifically, a disposable syringe having a 1 mm diameter needle hole was used to simulate the functions of a spinneret that may be used in commercial equipment for spinning rayon filaments. The Sample 1 viscose was forced through the syringe into an acidic wet bath to regenerate or produce a rayon filament. Specifically, the solution in this acidic bath contained 20% H<sub>2</sub>SO<sub>4</sub>.

(sulfuric acid), 10% Na<sub>2</sub>SO<sub>4</sub> (sodium sulfate), and 10% ZnCl<sub>2</sub> (zinc chloride). The Sample 2 viscose also was forced through the syringe into a similar acidic bath to produce a PTFE-enhanced rayon filament.

After these rayon filaments were formed they were each subject to a "drawing" procedure. Specifically, each of the freshly regenerated rayon filaments was stretched (while the cellulose chains were still relatively mobile) by holding them with pairs of tweezers. Visual observations indicated that the PTFE-enhanced rayon filament (Sample 2) stretched more the Sample 1 rayon filament that did not contain PTFE. After this drawing or stretching test, both freshly regenerated rayon filaments were washed with water several times and dried.

Both rayon filaments were then analyzed using multiple laboratory analytical techniques. In one analysis, the filaments were analyzed using Fourier Transform Infrared Spectroscopy (FTIR). The FTIR spectra confirmed that the two laboratory produced filaments were indeed rayon. The FTIR spectra of the PTFE-enhanced rayon filament (Sample 2) did not show any distinctive PTFE peaks.

In another analysis, the rayon filaments were analyzed using differential scanning calorimetry (DSC). The DSC curves for the PTFE-enhanced rayon filament (Sample 2) showed small peaks corresponding to the presence of PTFE. Small peaks were observed at 328.6°C at first heat and at 329.7°C at second heat. From these peaks the values for  $\Delta H$  (enthalpy) were calculated to be 4.1 and 3.9 J/g, respectively. From these values, the amount of PTFE in the PTFE-enhanced rayon filament (Sample 2) was estimated be about 5% by weight.

In yet another analysis, both Samples of rayon filaments were subject to thermogravimetric (TGA) analysis. TGA curves for the PTFE-enhanced rayon filament (Sample 2) indicated the presence of PTFE at concentrations of about 5.3%.



**CLAIMS:**

1. A method for making a fiber, comprising:
  - preparing a viscose of soluble fiber-forming material;
  - 5 adding polytetrafluoroethylene (PTFE) material to the soluble fiber-forming material during the preparation of the viscose;
  - forcing the viscose having the added PTFE material through a spinneret into a wet bath to form the fiber.
- 10 2. The method of claim 1, wherein adding the PTFE material to the fiber-forming material comprises dispersing PTFE particles having a size less than about one micron into the viscose.
3. The method of claim 1, wherein adding the PTFE material to the fiber-forming material comprises adding PTFE powder that is dispersible to submicron particle size.
- 15 4. The method of claim 1, wherein adding the PTFE material to the fiber-forming material comprises adding an aqueous dispersion of PTFE powder that is dispersible to low micron particle size.
5. The method of claim 4 wherein the aqueous solvent dispersion of PTFE powder comprises about 20% to about 60% PTFE by weight.
- 20 6. The method of claim 1, wherein adding the PTFE material to the fiber-forming material comprises adding an organic solvent dispersion of PTFE powder that is dispersible to low micron particle size.
- 25 7. The method of claim 1, wherein adding the PTFE material to the fiber-forming material comprises dispersing PTFE particles that have a size smaller than a channel size of the spinneret.

8. The method of claim 1, wherein adding the PTFE material to the fiber-forming material comprises introducing dispersible PTFE powder in the form of a pelletized master batch.
9. The method of claim 8, wherein the master batch comprises about 5% PTFE to about 60% PTFE.
10. The method of claim 1, wherein the fiber-forming material comprises material selected from the group of cellulose, compounds of cellulose and any combination thereof.
11. ~~The method of claim 1, wherein preparing a viscose of fiber-forming material; comprise the steps of steeping, pressing, shredding, aging, xanatahation, dissolving, ripening, filtering, and degassing, and wherein adding polytetrafluoroethylene (PTFE) material to the fiber-forming material during the preparation of the viscose comprises adding PTFE during at least one of the steps in preparing the viscose.~~
12. The method of claim 1, wherein forcing the viscose having the added PTFE material through a spinneret into a solution to form the fiber, further comprises solidifying the forced viscose such that the PTFE particles are dispersed substantially through out the body of the fiber.
13. A fabric comprising fibers made by the method of claim 1.
14. A synthetic fiber, comprising:
  - a wet spun extrusion of cellulose material; and
  - a dispersion of PTFE particles in the wet spun extrusion.
15. The synthetic fiber of claim 14 wherein the PTFE particles are distributed substantially homogeneously through the wet spun extrusion.

16. The synthetic fiber of claim 14 wherein the dispersion of PTFE particles comprises PTFE particles having a size less than about one micron.
17. A fabric comprising the synthetic fiber of claim 14.
18. An article of manufacture comprising the synthetic fiber of claim 14.

# INTERNATIONAL SEARCH REPORT

International application No.

PCT/US03/31263

## A. CLASSIFICATION OF SUBJECT MATTER

IPC(7) : D01F 2/02, 2/10, 6/12

US CL : 264/187, 188, 191, 211; 106/162.6, 166.6, 170.55, 195.1, 201.1

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 264/187, 188, 191, 211; 106/162.6, 166.6, 170.55, 195.1, 201.1

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5,762,846 A (BLANKENBECKLER et al) 09 June 1998 (09.06.1998), column 1, lines 5-10 and 20-25; column 2, lines 23-41; column 7, lines 21-33; column 9, lines 49-67.	1-18

☐ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

\* Special categories of cited documents:

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier application or patent published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T"

later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X"

document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y"

document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&"

document member of the same patent family

Date of the actual completion of the international search

04 February 2004 (04.02.2004)

Date of mailing of the international search report

25 FEB 2004

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**INTERNATIONAL SEARCH REPORT**

PCT/US03/31263

**Continuation of Item 4 of the first sheet:**  
The title is too long (PCT Rule 4.3).

The new title is: PROCESS OF MAKING CELLULOSIC FIBERS INCLUDING PTFE